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(72) Inventors JAMES RICHARD KNIGHT and PETER STEEL

lead + tin

(54) IMPROVEMENTS IN OR RELATING TO SOFT-SOLDER COATED WIRE, STRIP OR TAPE

(71) We, ENGELHARD INDUSTRIES LIMITED, a British Company, of St. Nicholas House, St. Nicholas Road, Sutton, Surrey, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of preparing a soft-soldered coated electrically conductive wire, strip or tape.

In the manufacture and assembly of electronic and electrical devices, such as resistors and printed circuits, it is frequently desirable to use conductor wires which are provided with a surface coating of a low melting point solder alloy such as a solder alloy of lead and tin. For example, it is customary for electrical resistors to be provided with soft-soldered coated current lead-out wires so that, when the electrical resistor is incorporated in an electrical or electronic device, effecting electrical connection using soft-solder is facilitated by the coating already present on the current lead-out wire.

Hitherto, soft-solder coated wires have been produced by one of two processes. In an early method the conductor wire, for example a pure copper wire, is coated with a layer of lead-tin alloy by passing the wire through a bath of the molten lead-tin alloy. This process is not entirely satisfactory since in practice it has been found difficult to maintain a continuous surface coating of uniform thickness and soldering behaviour on the wire. In a more recent and more satisfactory process, the lead-tin alloy is applied to the conductor wire by a continuous electrodeposition method using an electrolyte comprising an aqueous solution containing lead and tin fluoborates and using anodes made of a lead-tin alloy. In the electrodeposition process used hithertofor, the tank in which the electrodeposition of the lead-tin alloy solder coating is carried out is provided with an electrolyte containing suitable soluble compounds of both lead and tin and with anodes of a lead-tin alloy of the same composition as that required to form the coating on the conductive member. When it is desired to alter the composition of the lead-tin alloy coating, it was previously necessary to change the electrolyte and the anode, such changes necessitating the complete stoppage of the continuous electro-plating equipment for a considerable period of time.

Naturally, it is desired that the soft-solder coated wire is readily solderable not only immediately after coating, but also after storage subsequent to coating, which storage may be for a relatively long period of time. It is equally important that the solderability of the wire should not deteriorate as a result of any process carried out during the manufacture of any component of which it forms part, since otherwise the subsequent incorporation of the component into a circuit by soldering would be rendered difficult. An example of such a process is the manufacture of electrical resistors, during which process the resistor and the soft-solder coated current lead-out wire must normally be exposed to comparatively high temperatures, of the order of 220°C, for relatively long periods. Experience has shown that the solderability of soft-solder coated lead-out wires exposed to such a treatment is impaired.

In accordance with the present invention, it has been found that it is not necessary for a soft-solder coating to be deposited on the surface of a conductor in the form of an alloy or intimate mixture and that good soldering characteristics are obtained if the coating is applied in separate distinct layers. The main advantage of the method of the invention is the ease with which soft-solder coatings of different compositions may be obtained, although it has been found that in some cases a lead-tin coated copper conductor wire is more resistance to deterioration as a result of exposure of heat if the lead-tin coating is applied in two layers, the first, being of lead,

being in direct contact with the copper and the outermost layer being of tin. It is believed that this improvement is due to the fact that the layer of lead acts as a diffusion barrier between the copper and the tin during exposure to heat, thereby preventing the formation of an intermetallic compound between the copper and the tin. A coated wire having an outermost layer formed of tin is superior to one prepared by either of the prior art processes since the coated wire has a much higher corrosion resistance than a conventional coated wire, the corrosion resistance of tin being higher of that of either lead or of a lead-tin alloy. Accordingly, such coated wires are such less prone to surface deterioration in storage than conventional solder-coated wire.

Hence, in accordance with the present invention there is provided a method of preparing a soft-solder coated electrically conductive wire, strip or tape, which comprises successively electrodepositing onto the surface of the wire, strip or tape at least one layer of lead or a mixture of a major amount of lead and a minor amount of tin, and at least one layer of tin or mixture of a major amount of tin and a minor amount of lead.

Advantageously there is successively electrodeposited onto the surface of the wire, strip or tape at least one layer of lead and at least one layer of tin.

The invention also provides an electrical component having as its electrical connections, soft-solder coated wire, strip or tape prepared by the method described above, e.g. a resistor having, as its lead wires soft-solded coated wire prepared by the method described above.

The invention further provides the method of joining electrical components together by the application of molten soft-solder thereto, wherein there is used at least one component which is, or which is provided with, a soft-solder coated wire, strip or tape prepared by the method described above.

In accordance with the method of the invention, the coating applied to the wire, strip or tape is preferably a lead-tin coating with a layer of lead adjacent to the wire, strip or tape. Such a lead-tin coated wire, strip or tape may be more resistant to deterioration as a result of exposure to heat, and also may be more resistance to deterioration during storage, than any similar wire, strip or tape available hitherto.

As previously indicated, control of the composition of the coating is not easy in the known electrodeposition method, since it is effected by a number of factors, amongst which are, for example, electrolyte composition, anode composition, temperature and current density. However, in the method of the present invention, the composition of the total coating may be readily controlled by, for example, simple adjustment of the electroplating current controls to vary the relative amount of lead and tin separately electrodeposited onto the wire, strip or tape.

In practice, the wire, strip or tape to be coated by the method of the present invention is passed through a series of tanks which include those for the preliminary cleaning and rinsing operations, followed by those containing the electrolyte and finally those for the final rinsing operations.

In the method of the present invention, the wire, strip or tape is first passed through cleaning and rinsing tanks as in the conventional electrodeposition method, and is then passed through a first electro-plating tank having anodes of pure lead and containing an electrolyte of a suitable lead compound, and through a second electro-plating tank having anodes of pure tin and containing an electrolyte of a suitable tin compound. The wire, strip or tape is then passed through the final rinsing tank, as in the conventional electrodeposition process. The amount of current supplied to each tank is separately controlled and it is therefore possible to control the relative amounts of both lead and tin electrodeposited. Hence the overall composition of the lead-tin coating can be controlled whilst the electrodeposition equipment is being used. It is the main advantage of the method of the present invention that the composition of the soft-solder coating may be altered at will by merely adjusting the electrical current supplied to each of the tanks, without stopping the process to change either the electrolyte or the anodes.

In accordance with the invention, it is possible to electrodeposit onto the surface of the electrically conductive wire, strip or tape layers of a mixture of a major amount of tin and a minor amount of lead, and layers of a major amount of lead and a minor amount of tin. Thus, for example, a first layer of lead-tin could be formed using an electrolyte containing a lead compound and a minor amount of a tin compound, and a second layer could be formed on the first layer using an electrolyte containing a tin compound and a minor amount of a lead compound.

After depositing the solder coating onto the wire, strip or tape the wire, strip or tape can be subjected to an ageing process to improve the solderability thereof, the improvement depending upon the severity of the ageing process used.

Whilst the method of the present invention is particularly advantageous for the preparation of lead-tin coatings on copper and copper alloy wires, by virtue of the freedom from formation of undesirable tin-copper compounds when the lead layer is adjacent to the copper, the method of the present invention possesses advantages in the case of other base metal wires required to have lead-tin coatings. The advantages of greater resistance to

corrosion, easy control of the compositions of the soft-solder coating and particularly the simplicity and cheapness of the method whereby the composition of the soft-solder coating may be changed are applicable whatever the base metal upon which the coating is electrodeposited.

The following Examples illustrate the method of the present invention.

EXAMPLE 1

A length of copper wire, 0.032 inches in diameter, was electroplated in a continuous wire plating plant by effecting the following six steps:—

1.1 Electrolytic cleaning in a phosphate-carbonate-hydroxide aqueous cleaning solution containing 7 g/l of NaOH, 14 g/l of Na_2CO_3 and 7 g/l of Na_3PO_4,
1.2 Rinsing in water,
1.3 Pickling in 25% aqueous fluoboric acid solution,
1.4 Rinsing water,
1.5 Electroplating, at a current density of 420 amperes per square foot, using a mixed lead-tin fluorborate electrolyte solution containing 200 g/l of $Pb(BF_4)_2$, 50 g/l of $Sn(BF_4)_2$, 200 g/l of HBF_4 and 12 g/l of resorcinol, and anodes of a lead-tin alloy containing 30% by weight of tin, to give a lead-tin alloy coating on the wire, and
1.6 Rinsing in water.

The conditions were controlled during the electroplating in such a way that the thickness of the lead-tin alloy coating was 0.000160 inches (4.06 μ) and had a composition of 70 percent by weight of lead and 30 percent by weight of tin. This length of coated wire was designated Sample A.

A second length of coper wire, 0.032 inches in diameter, was electrolyically cleaned and then pickled, as in steps 1.1, 1.2, 1.3 and 1.4 above, and was then coated with a layer of pure lead follower by a layer of pure tin, by passing the wire through a first electroplating tank having pure lead anodes and containing an electrolyte comprising 200 g/l of $Pb(BF_4)_2$, 200 g/l of HBF_4 and 12 g/l of resorcinol, at a current density of 300 amperes per square foot, and a second electroplating tank having pure tin anodes and containing an electrolyte comprising 200 g/l of $Sn(BF_4)_2$, 150 g/l of $LiBF_4$ and 12 g/l of resorcinol, at a current density of 400 amperes per square foot. Step 1.6 was then effected. The electroplating conditions were adjusted so that the thickness of the lead coating was 0.000102 inches (2.59 μ) and the thickness of the tin coating was 0.000058 inches (1.47 μ). The overall composition of the coating was 70% weight of lead and 30% by weight of tin. This length of wire was designated Sample B. It will be observed that both Samples A and B were provided with the same overall thickness of lead-tin coating and that the overall composition was in both cases 70% by weight of lead and 30% by weight of tin.

Both samples were subjected to ageing treatments at elevated temperatures and were then tested for solderability by the procedure laid down in British Standard No. 2011, 1966, Part 2T, Method 3 and the results are shown in the following table:

TABLE

Sample	Ageing Temperature (°C)	Ageing Time (hours)	Soldering Time (seconds)
A	165	5.0	1.2
B	165	5.0	0.4
A	180	3.0	1.7
B	180	3.0	0.5
A	200	1.5	1.3
B	200	1.5	0.6
A	225	1.25	1.5
B	225	1.25	0.7
A	200	1.0	0.6
B	200	1.0	0.5
A	200	2.0	1.2
B	200	2.0	0.6

It will be seen from the table that in every case Sample B, which was coated by the method of the present invention, showed a shorter soldering time than Sample A, which was prepared by a conventional electrolytic coating process.

EXAMPLE 2

This Example shows the ease with which variations in the composition of the solder coating may be obtained in accordance with the invention.

The procedure described in Example 1 for applying a first layer of lead and a second layer of tin to the copper wire was repeated with three different lengths of copper wire, the following electroplating conditions being used:

(a) Formation of layer of lead:

current	6.0 amps
current density	45 amps/dm^2
speed of wire	120 m/hour

Formation of layer of tin:

current	9.0 amps
current density	10 amps/dm^2
speed of wire	3000 m/hour

The overall composition of the lead-tin coating thus formed was 95% by weight of lead and 5% by weight of tin. The layer of lead had a thickness of 0.00015 inches (3.7 μ) and the layer of tin had a thickness of 0.000012 inches (0.3 μ).

(b) Formation of layer of lead:

current	4.5 amps
current density	3 amps/dm
speed of wire	120 m/hour

Formation of layer of tin:

current	33 amps
current density	40 amps/dm^2
speed of wire	3000 m/hour

The overall composition of the lead-tin coating thus formed was 70% by weight of lead and 30% by weight of tin. The layer of lead had a thickness of 0.000087 inches (2.2 μ) and the layer of tin had a thickness of 0.000071 inches (1.8 μ).

(c) Formation of layer of lead:

current	2.0 amps
current density	13.5 amps/dm^2
speed of wire	120 m/hour

Formation of layer tin:

current	80 amps
current density	100 amps/dm
speed of wire	3000 m/hour

The overall composition of the lead-tin coating thus formed was 40% by weight of lead and 60% by weight of tin. The layer of lead had a thickness of 0.000035 inches (0.9 μ) and the layer of tin had a thickness of 0.00012 inches (3.1 μ).

It can be seen that variations in the compositions of the coating can be readily obtained by employment of the method of the invention.

WHAT WE CLAIM IS:—

1. A method of preparing a soft-solder coated electrically conductive wire, strip or tape, which comprises successively electrodepositing onto the surface of the wire, strip or tape at least one layer of lead or a mixture of a major amount of lead and a minor amount of tin, and at least one layer of tin or a mixture of a major amount of tin and a minor amount of lead.

2. A method of preparing a soft-solder coated electrically conductive wire, strip or tape, which comprises successively electrodepositing onto the surface of the wire, strip or tape at least one layer of lead and at least one layer of tin.

3. A method according to claim 2, in which a layer of lead is electrodeposited onto the surface of the wire, strip or tape and a layer of tin is electrodeposited onto the surface of the layer of lead.

4. A method according to any one of the preceding claims, in which the wire is copper wire.

5. A method in accordance with claim 2 for the preparation of a soft-solder coated wire, substantially as described in the foregoing Example 1 or Example 2.

6. A soft-solder coated wire, strip or tape whenever prepared by the method claimed in any one of the preceding claims.

7. An electrical component having, as its electrical connections, soft-solder coated wire, strip or tape as claimed in claim 6.

8. A resistor having, as its lead wires, soft-solder coated wire as claimed in claim 6.

9. The method of joining electrical components together by the application of molten soft-solder thereto, wherein there is used at least one component which is, or which is provided with, a soft-solder coated wire, strip or tape as claimed in claim 6.

10. A method according to claim 9, wherein there is used at least one electrical component which is a resistor as claimed in claim 8.

HASELTINE, LAKE & CO.,
Chartered Patent Agents,
28, Southampton Buildings,
Chancery Lane,
London, W.C.2A 1AT.
Agents for the Applicants.

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